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# Thermal Conductivity Modeling of Refrigerant Mixtures in a Three-Parameter Corresponding States Format[1]

**G. Scalabrin,[2,3] L. Piazza,[2] M. Grigiante,[4] and M. Baruzzo[2]**

A predictive model for the thermal conductivity (TC), in a corresponding states (CS) format, is proposed here for mixtures of homologous fluids such as the *halogenated alkanes* (HA) and the *alkanes* (A), most of which are used as refrigerants. The predictive nature of the model originates from a new study carried out for the TC of pure fluids. For the dilute-gas term the model requires an individual correlation for each component, whereas for the excess contribution the model structure makes use of TC dedicated equations (TCDEs) of two reference fluids, which in this work are *methane* and $R134a$. The mixture model adopts specific mixing rules for each of the two TC contribution terms: the dilute-gas term $\lambda_{0\text{mix}}$ is obtained from the Mason and Saxena mixture model, while the excess term $\Delta_E\lambda_{\text{mix}}$ is determined from the Wong et al. mixing rules in the *one fluid model* approach. Setting the mixing rules interaction coefficients to unity, the resulting model presents a completely predictive character. The model has been tested on both liquid and vapor phases of the following systems: R32/R125, R32/R134a, R125/R134a, R404a, and R32/R134/R125. For a total of 1223 experimental points in the liquid phase, the overall AAD is 5.39%, while for a total of 2358 points in the vapor phase, the AAD is 2.62%. These predictive mode performances can then be regarded as particularly satisfactory and are of a level similar to the claimed experimental uncertainty. An improved version of the model is also proposed for modeling azeotropic mixtures. The results reached in this case for a total of 1989 experimental points give an average AAD of 5.30%. Considering both the predictive nature and the simple computational procedure of the model, it significantly enhances the calculations of the TC of mixtures.

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[2] Dipartimento di Fisica Tecnica, Università di Padova, via Venezia 1, I-35131 Padova, Italy.

[3] To whom correspondence should be addressed. E-mail: gscala@unipd.it

[4] Dipartimento di Ingegneria Civile Ambientale, Università di Trento, via Mesiano 77, I-38050 Trento, Italy.

**KEY WORDS:** alkanes; dedicated equations; halogenated alkanes; mixtures, predictive model; thermal conductivity; three-parameter corresponding states; transport properties.

## 1. INTRODUCTION

A knowledge of the thermophysical properties of fluids has increased significantly in recent years specifically regarding the applications of new working fluid mixtures in many engineering fields. The relevant number of possible chemical mixtures and the versatility of operating conditions more often require a modeling approach based on prediction schemes rather than on experimental data.

Existing predictive thermal conductivity (TC) models for mixtures can be classified into two general groups. The models of the first group move from the kinetic theory of the dilute-gas and form the basis of an advanced approach recently developed by Schreiber, Vesovic, and Wakeham (SVW) [1] which enables prediction of the TC of gaseous mixtures by an expansion vectors theory. The model of Mason, Saxena, and Wassiljewa (MSW) [2], which also belongs to this group, extends the previous work of Wassiljewa [3] to polyatomic mixtures introducing consistent approximations to the kinetic theory to obtain a simple calculation procedure for the TC of monatomic mixtures. Even though this model is dated, it is widely used to analyze experimental TC data and for engineering design purposes. A higher accuracy is however reached by the SVW model, as shown in a recent study of Vesovic [4] for mixtures having high precision data.

The second-group models originate from the corresponding states(CS) principle. Until now, models based on a three-parameter CS scheme have been successfully applied for thermodynamic properties [5–9] and for viscosity [10–13]. The proposed model extends the potential of CS assuming a fluid specific scaling parameter for TC [14]. The basic structure of the model is extended to mixtures using mixing rules in a predictive mode. New features include the use of selected dedicated equations for the model structure references, which allows extension of the model over wide ranges of the $\lambda TPx$ surfaces at liquid, vapor, and supercritical conditions. The mixture model is predictive and is particularly convenient when the paucity of experimental data requires the use of predictive methods.

## 2. PROPOSED MODEL

The basic structure of this model is built on the pure fluid TC model recently developed by the same authors [14]. The analysis of the "*conformality*" behavior applied to the TC surfaces $f(\lambda_r, P_r, T_r) = 0$ of pure fluids has shown that a general CS behavior cannot be recognized without separating the different contribution terms of the TC which are the dilute-gas term $\lambda_0(T)$, the residual function $\Delta_R\lambda(\rho, T)$, and the critical enhancement function $\Delta_R\lambda(\rho, T)$. The behaviors of these terms were studied separately to demonstrate the influence of each term. The structure of the pure fluid model was then set up adding these different contributions, and such a format is likewise maintained for mixtures. To extend the model to mixtures, specific mixing rules are assumed for each of the contributions following the "*one fluid model*" technique.

## 2.1. Mixture Model for the Dilute-Gas Term

As a result of the pure fluid conformality behavior analysis [14], the dilute-gas term contributions cannot be represented in a general form and, as a consequence, these terms have to be individually set up for each fluid. The mixture dilute-gas term can be simply obtained by "mixing" the corresponding contributions of the pure fluids through suitable mixing rules. Analyzing different dilute-gas methods for mixtures [4], focusing in particular on the maximum reduction of the input properties for the pure species, it was concluded that the least demanding method is the MSW [2], which is here interpreted as

$$\lambda_{0\mathrm{mix}}(T, \bar{x}) = \sum_{i=1}^{N} \frac{y_i \lambda_{0i}}{\sum\limits_{i=1}^{N} y_i \Phi_{ij}} \tag{1}$$

with

$$\Phi_{ij} = \frac{\varepsilon_{ij}\left[1 + (\lambda_{0i}/\lambda_{0j})^{1/2} (M_i/M_j)^{1/4}\right]^2}{\left[8\,(1 + M_i/M_j)\right]^{1/2}} \tag{2}$$

where $\lambda_{0i}$ is the dilute-gas term of the $i$th fluid, among the $N$ mixture components, and $M_i$ is the corresponding molar mass. It was found that, for the systems studied here, the best choice for the $\varepsilon_{ij}$ value is 1.0, whereas $\lambda_{0i}$ is directly calculated from the pure fluid dilute-gas term [14]. This means that such property is the only input requirement for this mixture term. In the case the model performance is unsatisfactory in a predictive mode; however, the $\varepsilon_{ij}$ can be used as a correlation parameter to tune the mixture model on the experimental data.

It has to be stressed that for this term a "*one fluid model*" approach cannot be assumed, as will be done for the excess term, and that, as a consequence, the accuracy level of this contribution strictly depends on the effectiveness of the adopted mixing rules.

### 2.2. Mixture Model for the Excess Term Contribution

The study of the TC conformality [14] can be used to define specific parameters to accurately describe the excess term contribution, which is defined by

$$\Delta_E\lambda(\rho,T)=\Delta_R\lambda(\rho,T)+\Delta_C\lambda(\rho,T) \tag{3}$$

where $\Delta_R\lambda(\rho,T)$ represents the residual term and $\Delta_C\lambda(\rho,T)$ is the critical enhancement; the excess term is then the additional part of TC with respect to the dilute-gas term.

Selecting a reference fluid, the TC scaling parameter $\kappa_i$ of a target fluid is

$$\kappa_i=\left(\Delta_E\lambda_r^{\mathrm{lsat}}\Big|_i-\Delta_E\lambda_r^{\mathrm{lsat}}\Big|_{\mathrm{ref}}\right)_{T_r} \tag{4}$$

where $\Delta_E\lambda_r^{\mathrm{lsat}}\big|_i$ is the excess TC of the fluid of interest referenced to saturated liquid conditions and expressed in reduced form, $\Delta_E\lambda_r^{\mathrm{lsat}}\big|_{\mathrm{ref}}$ is the corresponding quantity for the reference fluid, in this case methane, while subscripts $E$ and $r$ refer to excess and reduced quantities, respectively. The $\Delta_E\lambda_r^{\mathrm{lsat}}\big|_i$ term is obtained from an experimental saturated liquid value at $T_r=0.75$, given the TC dilute-gas expression of the component, as from the general assumptions of the model [14].

As in Ref. [14], the reference fluid is methane, from whose TCDE the $\Delta_E\lambda_r^{\mathrm{lsat}}\big|_{\mathrm{ref}}$ term is calculated, whereas for the values of the $\kappa_i$ parameters of the studied fluids, reference is made to the former work [14].

Due to the uncertainty of measurements of the TC at the critical point, this quantity can be expressed in a reduced form only by introducing a specific pseudo-critical parameter $K_c$ defined as

$$K_c=\frac{R^{5/6}P_c^{2/3}}{T_c^{1/6}M^{1/2}A^{1/3}} \tag{5}$$

where $T_c$ is the critical temperature, $P_c$ is the critical pressure, $M$ is the molar mass of the fluid, $R$ is the universal gas constant, and $A$ is Avogadro's number. The reduced TC $\lambda_r$ of a given $\lambda$ value is then obtained from

$$\lambda_r=\frac{\lambda}{K_c} \tag{6}$$

Selecting two reference fluids among those studied, the excess term model for pure fluids is expressed by

$$\Delta_E \lambda_{ri}\left(T_r, \rho_r, \kappa_i\right) = \Delta_E \lambda_r^{r1} + \frac{\kappa_i - \kappa^{r1}}{\kappa^{r2} - \kappa^{r1}}\left(\Delta_E \lambda_r^{r2} - \Delta_E \lambda_r^{r1}\right) \tag{7}$$

where $\Delta_E \lambda_r^{r1}$ and $\Delta_E \lambda_r^{r2}$ are the excess contributions of the reference fluids in reduced form. Here the superscripts $r1$ and $r2$ stand for the first and second reference fluids, respectively, and are calculated from the TCDEs of two selected reference fluids. To preserve a procedure consistent with the proposed one for the pure fluids [14], the same references (*methane* and $R134a$) are also maintained here. For their TCDEs reference is made to the original publications for methane [15] and for R134a [16].

In a common formulation of a dedicated equation the TC is expressed as a function of temperature and density. The excess term for the reference depends on the same variables and, in reduced form, it is, $\Delta_E \lambda_r^{ri}\left(\rho_r^{ri}, T_r\right)$, where $\rho_r^{ri}$ and $T_r$ are the reduced density and temperature of the reference fluid $ri$.

However, in a reduced variables format, the independent variables are $T_r$ and $P_r$, but to solve the equation $\Delta \lambda_r^{ri}\left(\rho_r^{ri}, T_r\right)$ the reference fluid reduced density $\rho_r^{ri}$ has to be known from the solution of its equation of state $P_r = P_r\left(T_r, \rho_r^{ri}\right)$. The required procedure is then expressed by the set of equations,

$$\begin{cases} P_r = P_r\left(T_r, \rho_r^{ri}\right) \\ \Delta_E \lambda_r^{ri} = \Delta_E \lambda_r^{ri}\left(\rho_r^{ri}, T_r\right) \end{cases} \tag{8}$$

The procedure has to be applied to each of the reference fluids r1 and r2 iteratively solving the system Eq. (8) to give, at defined $T_r$ and $P_r$ values, the density $\rho_r^{ri}$ and the excess TC term $\Delta_E \lambda_{ri}$ of the fluid of interest in reduced form. Such procedure can be similarly maintained also for mixtures; in fact, in a CS format the *one fluid model* approach requires only determination of the pseudo-critical parameters of the mixtures $T_{c\text{mix}}$ and $P_{c\text{mix}}$ as substitutes for the components' critical parameters $T_c$ and $P_c$.

The classical method, common to CS techniques, of modifying the critical properties of the components by suitable mixing rules, is obtained here by a rearrangement of the mixing rules of Wong et al. [17], also previously tested for mixture viscosity modeling [13]. The original form has been maintained in this work while only substituting for the acentric factor $\omega$ with the new TC specific scalar parameter $\kappa_i$ previously defined. The proposed mixing rules are

$$T_{c\mathrm{mix}}/P_{c\mathrm{mix}} = \sum_i \sum_j x_i x_j T_{cij} T_{cij} / P_{cij} \tag{9}$$

$$T^2_{c\mathrm{mix}} P_{c\mathrm{mix}} = \sum_i \sum_j x_i x_j T^2_{\mathrm{c}ij} / P_{\mathrm{c}ij} \tag{10}$$

$$T_{\mathrm{c}ij} = \eta_{ij} \left(T_{\mathrm{c}i} T_{\mathrm{c}j}\right)^{1/2} \tag{11}$$

$$P_{\mathrm{c}ij} = 8T_{\mathrm{c}ij} \Big/ \left[(T_{\mathrm{c}i}/P_{\mathrm{c}i})^{1/3} + \left(T_{\mathrm{c}j} P_{\mathrm{c}j}\right)^{1/3}\right]^3 \tag{12}$$

$$\kappa_{\mathrm{mix}} = \sum_i x_i \kappa_i \tag{13}$$

where the subscript $c$ refers to the critical value of each component, and $\eta_{ij}$ is an adjustable interaction parameter.

These equations enable determination of the pseudo parameters $T_{c\mathrm{mix}}$ and $P_{c\mathrm{mix}}$ through which the reduced variables $T_r$ and $P_r$, at the actual $T$ and $P$ values of the mixture, are calculated as

$$T_r = T/T_{c\mathrm{mix}}, \quad P_r = P/P_{c\mathrm{mix}} \tag{14}$$

The excess contribution of the reference fluids is then determined following the same steps previously summarized in the system of Eq. (8). As a goal of a three-parameter CS method is to calculate the property of a mixture by interpolating those of the references at the same $T_r$ and $P_r$ values, the model proposed for pure fluids, Eq. (7), can be likewise extended to mixtures adopting the mixture scaling parameter $\kappa_{mix}$ determined from Eq. (13). The final structure of the model for the excess TC contribution is then

$$\Delta_E \lambda_{r\mathrm{mix}} (T_r, P_r, \bar{x}) = \Delta_E \lambda_r^{r1} + \frac{\kappa_{\mathrm{mix}} - \kappa^{r1}}{\kappa^{r2} - \kappa^{r1}} \left(\Delta_E \lambda_r^{r2} - \Delta_E \lambda_r^{r1}\right) \tag{15}$$

## 2.3. General Structure of the Mixture Thermal Conductivity Model

The excess term obtained in reduced form by Eq. (15) can be expressed as a function of the common T,P, and $\bar{x}$ variables, which is the real excess term of the mixture conductivity,

$$\Delta_E \lambda_{\mathrm{mix}} (T, P, \bar{x}) = K_{c\mathrm{mix}}\, \Delta_E \lambda_{r\,\mathrm{mix}} (T_r, P_r, \bar{x}) \tag{16}$$

where the constant parameter $K_{c\mathrm{mix}}$ has the same formulation as in Eq. (5) but referred, in this case, to the pseudo-critical parameters

$$K_{c\mathrm{mix}} = \frac{R^{5/6} P^{2/3}_{c\mathrm{mix}}}{T^{1/6}_{c\mathrm{mix}} M^{1/2}_{\mathrm{mix}} A^{1/3}} \tag{17}$$

Knowing the dilute-gas term of the mixture $\lambda_{0\text{mix}}$from the ideal part of the model, Eq. (1), and the excess term contribution $\Delta_E\lambda_{\text{mix}}$ from the proposed model, Eq. (16), the TC of the mixture can be finally determined through the classical formulation as

$$\lambda_{\text{mix}}\,(T,\,P,\bar{x})=\lambda_{0\text{mix}}\,(T,\bar{x})+\Delta_E\lambda_{\text{mix}}\,(T,\,P,\bar{x}) \tag{18}$$

It is particularly interesting to note that the model does not require the density of the mixture as input data and that the variables are the $T, P$ and $\bar{x}$ values of the mixture of interest. Only the dedicated equations of state and the TCDEs of the references, together with the dilute-gas term individual correlations for the components, are then required for the mixture model, whereas no correlation has to be known for the mixture.

According to the validity ranges of TCDEs of the reference fluids, the model is applicable in the temperature ranges $0.734 \leqslant T_r \leqslant 0.99$ below the critical isotherm and $1.01 \leqslant T_r \leqslant 1.095$ above the critical isotherm, while the pressure range is up to $P_r = 17.258$.

Returning to the mixing rules, Eqs. (9)–(13), the adjustable interaction parameter $\eta_{ij}$ can be regressed on some sets of TC experimental data; in this case the model becomes *correlative*. Alternatively, if these coefficients are set to unity, the application of the model, Eq. (15), requires only the critical parameters $T_c$, $P_c$, and the scaling parameter $\kappa_i$ of the mixture components. With these assumptions the mixture model becomes totally *predictive*. The CS technique is particularly suitable for a predictive approach and for most of the investigated mixtures the results obtained refers to applications of the model in the *predictive mode*.

It is necessary to stress that in the vapor region the dilute-gas term of the mixture model has a greater portion of the total, whereas in the liquid region this is true for the excess term. For the case when the mixture model fails in representing data in one or both of these two regions, the model has to be arranged with tuning of the corresponding TC terms through the specific interaction parameter, $\varepsilon_{ij}$ for the dilute-gas and $\eta_{ij}$ for the excess term, with respect to experimental data. Whenever both terms have to be tuned, it is necessary to tune first the dilute-gas term, from which to generate the excess corresponding values of the experimental points. Then, it is possible to correlate the excess TC term on the so determined excess values.

A specific discussion will be proposed for selected examples of mixtures for which the regression of the interaction coefficients significantly improved the results of the model.

## 3. MODEL VALIDATION

The results from the model are summarized in Tables I, and II and refer to data sources presently available for the TC of halogenated alkanes mixtures. The validity range of the model, resulting from those of the reference equations, hinders the utilization of all experimental data for each of the sources. Those data effectively used for validation are cited as "*inside range*". Due to the present context and considering these constraints, it does not seem consistent to weight the data on the basis of their claimed experimental quality; as a consequence, without a preliminary screening, the obtained results can be substantially affected by the experimental uncertainty.

Different from the pure fluids TC modeling [14], where a comparison with TCDEs for a couple of fluids was performed to test the present model reliability, for mixtures neither TCDEs nor primary data from dedicated TC equation regression are available, so that the present validation cannot be substantially extended for a further quality check. Also, from a general analysis of the model performance, it emerges that the results are strictly dependent on the thermodynamic behavior of the mixtures so that it becomes appropriate to distinguish between *regular* (non-azeotropic) and *azeotropic* mixtures.

**Table I.** Validation Results for Regular Mixtures of Haloalkanes

| Mixture | Phase | NPT | NPT inside range | Range $T$ (K) | Range $P$ (MPa) | AAD (%) | Bias (%) | Max (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| *Liquid phase* | | | | | | | | | |
| R32/R134a | l | 84 | 36 | 272.8–316.1 | 2.00–30.00 | 3.80 | 3.01 | 7.56 | [18] |
| R32/R134a | l | 309 | 282 | 270.6–360.7 | 0.59–11.69 | 3.53 | −0.07 | 11.13 | [19] |
| R32/R134a | l | 120 | 65 | 273.2–323.2 | 2.00–20.00 | 4.76 | 1.71 | 9.89 | [20] |
| R125/R134a | l | 147 | 82 | 272.4–324.1 | 2.00–20.00 | 1.46 | 1.28 | 3.28 | [21] |
| R125/R134a | l | 278 | 242 | 256.8–347.0 | 0.48–9.95 | 3.72 | 1.81 | 15.59 | [19] |
| R32/R125/R134a | l | 168 | 166 | 272.7–324.2 | 2.00–20.00 | 12.89 | −5.11 | 35.61 | [22] |
| R32/R125/R134a | l | 357 | 320 | 269.7–345.4 | 0.42–12.26 | 5.58 | 4.68 | 11.29 | [19] |
| R32/R125/R134a | l | 44 | 16 | 272.8–298.7 | 2.0–30.0 | 9.27 | 8.88 | 11.68 | [23] |
| R404A | l | 24 | 14 | 273.7–322.8 | 2.00–20.00 | 6.99 | 6.99 | 8.31 | [24] |
| Overall liquid | | 1531 | 1223 | | | 5.42 | 1.33 | 35.61 | |
| *Vapor phase* | | | | | | | | | |
| R32/R134a | v | 998 | 923 | 264.4–348.0 | 0.08–0.57 | 3.36 | −3.35 | 9.88 | [19] |
| R125/R134a | v | 815 | 792 | 258.2–345.8 | 0.07–0.63 | 1.48 | 0.24 | 5.10 | [19] |
| R32/R125/R134a | v | 681 | 643 | 261.2–346.9 | 0.08–0.53 | 2.98 | −2.98 | 8.03 | [19] |
| Overall vapor | | 2494 | 2358 | | | 2.62 | −2.04 | 9.88 | |
| Overall liq. + vap. | | 4025 | 3581 | | | 3.58 | −0.89 | 35.61 | |

**Table II.** Validation Results for the Azeotropic Mixtures R32/R125, R134a/R290, and R32/R290[a]

| | | | | | Predictive mode | | | Correlative mode | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Phase | NPT | NPT inside range | Range T (K) | Range P (MPa) | AAD (%) | Bias (%) | Max (%) | AAD (%) | Bias (%) | Max (%) | Ref. |
| | | | | | | R32/R125 | | | | | |
| v | 69 | 69 | 283.1–298.1 | 0.10–1.20 | 1.82 | 0.41 | 4.56 | – | – | – | [25] |
| l | 60 | 28 | 283.2–298.2 | 0.10–1.20 | 5.27 | 4.95 | 10.65 | – | – | – | [18] |
| l | 168 | 98 | 272.4–324.0 | 2.0–20.0 | 3.78 | 0.86 | 12.58 | – | – | – | [26] |
| Overall | | 195 | | | 3.30 | 1.29 | | – | – | – | |
| | | | | | | R134a/R290 | | | | | |
| | | | | | | | | | Regression on liq. only:<br>$\varepsilon = 1$<br>$\eta_{ij} = 0.880027$ | | |
| v | 570 | 479 | 273.0–348.5 | 0.08–0.74 | 2.44 | −1.62 | 7.68 | 2.47 | −1.85 | 7.77 | [19] |
| l | 303 | 241 | 273.1–346.6 | 1.12–10.09 | 15.13 | 13.78 | 25.66 | 5.64 | 0.37 | 37.30 | [19] |
| Overall | 720 | | 6.68 | 3.53 | | 3.53 | −1.11 | | | | |
| | | | | | | R32/R290 | | | | | |
| | | | | | | | | | Regression on vap. and liq.:<br>$\varepsilon = 0.700222$<br>$\eta_{ij} = 0.908386$ | | |
| v | 951 | 801 | 265.9–341.3 | 0.08–3.24 | 9.00 | −7.49 | 61.10 | 5.56 | 3.97 | 14.33 | [19] |
| l | 307 | 273 | 269.8–346.9 | 1.17–10.75 | 17.01 | 12.24 | 45.58 | 10.71 | 3.23 | 52.57 | [19] |
| Overall | | 1074 | | 11.04 | −2.47 | | 6.87 | 3.78 | | | |
| Overall azeo | | 1989 | | 8.70 | −3.47 | | 5.30 | 1.82 | | | |

[a] R290 is the standard designation for the refrigerant propane.

### 3.1. Regular Mixtures

In Table I the results for regular binary mixtures R32/R134a and R125/R134a are reported for both liquid and vapor regions. Also, the ternary R32/R125/R134a mixture has been investigated in both liquid and vapor regions and the R404A mixture in the liquid region.

The results are particularly satisfactory for the vapor phase where, in a predictive mode, the average absolute deviation (AAD) of 2.62%, based on a total of 2358 data points, is consistent with that claimed for the experimental uncertainty. Satisfactory results are also confirmed for the liquid phase, for which the overall AAD is 5.40% based on a total of 1223 points. Including vapor and liquid data the overall AAD for 3581 points is 3.57%. Considering the predictive mode of the model assumed for these cases, the results are consistent with the claimed experimental uncertainties and can thus be regarded as quite satisfactory. It is interesting to note that the number of TC sets for mixtures is relatively small and that those considered in this study probably represent all the data available for the non-azeotropic systems pertaining to the families of fluids studied here.

The error deviations of the model for some of these systems are reported as a function of mixture reduced temperature, i.e., $T/T_{c\text{mix}}$, in Figs. 1 & 2 for the liquid and vapor regions, respectively. For a number

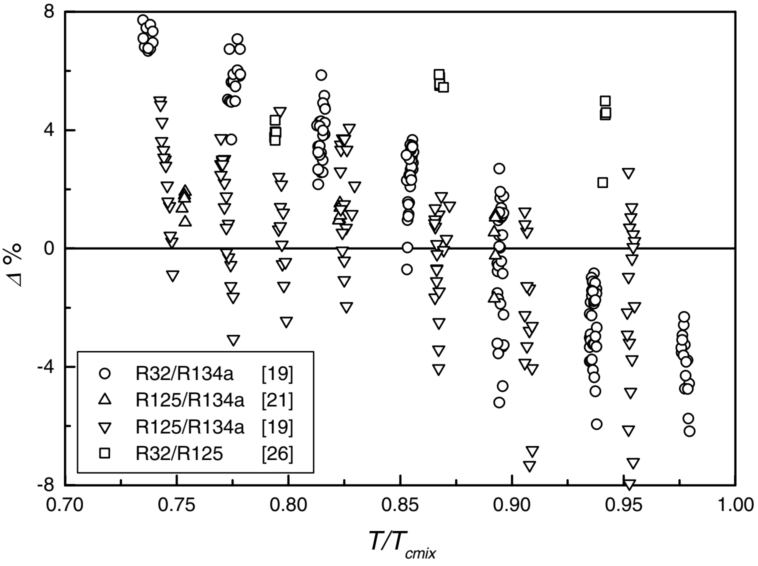

**Fig. 1.** Thermal conductivity deviations of mixtures of HAs in the liquid region as a function of $T_{r\text{mix}}$.

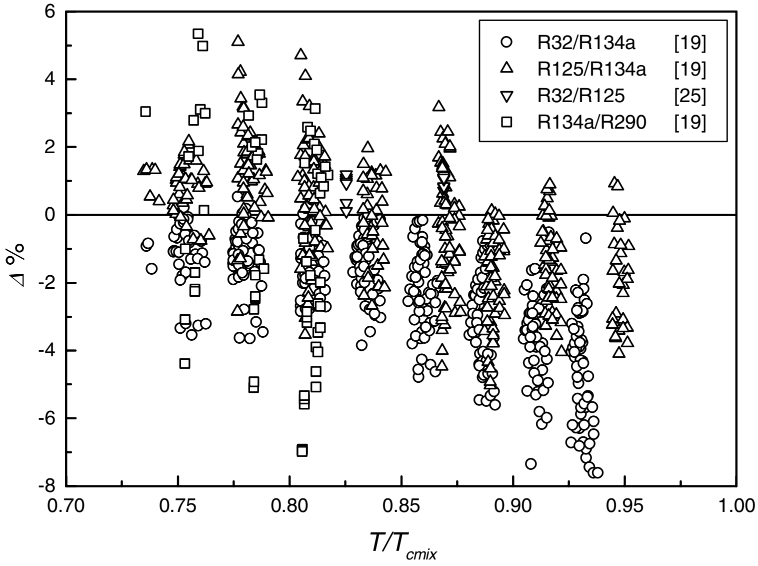

**Fig. 2.** Thermal conductivity deviations of mixtures of HAs in the vapor region as a function of $T_{r\text{mix}}$.

of systems the bias is shown to be practically absent for both fluid regions, and consequently, the scatter represents the experimental error noise. The error bands are furthermore similar for the two regions.

### 3.2. Azeotropic Mixtures

For azeotropic systems, the model in the predictive mode has demonstrated to have an uneven behavior, in fact, for systems with weak azeotropy the model may perform satisfactorily in the predictive mode, but for systems with increasing and pronounced azeotropy, the model shows a decrease in accuracy first for the liquid region and then also for the vapor region.

Unfortunately the number of such systems with available data is limited and this limits the possibility of a more detailed study. In Table II the results refer to the performances of the model applied to the three azeotropic mixtures R32/R125, R134a/R290, and R32/R290. Data are from Refs. [18,25,26] for R32/R125, and from Ref. [19] for the other two systems.

Whenever the model used in the predictive mode, either for the vapor phase or for the liquid phase, performs satisfactorily, the correlative mode is not applied and the corresponding entries in the table are left void. If, on the contrary, the correlations for one or both the phases are required, the correlative mode results are shown in the corresponding entries. So, for the system R32/R125 no correlation is needed, whereas for the system R134a/R290 the correlation mode is applied only for the mixture excess term, leaving the dilute-term contribution totally predictive. For the last system R32/R290, exhibiting a pronounced azeotrope, both of the model contributions were correlative. For the case of the correlative mode the interaction coefficients, $\varepsilon_{ij}$ and $\eta_{ij}$, obtained for each part of the model are reported in the corresponding entries of Table II.

The R32/R125 system exhibits a weak azeotrope for a composition shifted toward one of the components and, according to the general trend drawn from this work, its TC surface can be reliably modeled in a totally predictive mode. The AAD is 1.82% for the vapor data set and ranges from 3.78 to 5.27% for the liquid data sets. The R290/R134a system has a more pronounced azeotrope causing the TC in the liquid region to require tuning through the interaction coefficient regression for the excess term, whereas the vapor phase behaves quite satisfactorily in the predictive mode. The final result is then very good with an AAD of 2.44% for the vapor and of 5.64% for the liquid. The R32/R290 system is strongly azeotropic and its TC surface representation requires the tuning of both the dilute-gas term and the excess term, but after application of the interaction coefficients, the AAD reduces to 5.56 and 10.71% for the vapor and liquid phases, respectively.

As a general comment, it can be said that the obtained accuracy is better for the vapor phase than for the liquid phase and that for both phases the final performance for azeotropic systems has a level similar to that of the regular systems. In the liquid phase the precision is slightly lower due to the addition of the model dilute-gas and excess term residual errors. The final result for the model performance can be considered as very satisfactory, particularly considering that the deviations of the calculated values for over 6000 experimental points are comparable with the experimental uncertainties.

For the sake of completeness a comparison is also proposed for data for the mixtures R290/R134a and R32/R290 from Ref. [19]. The authors of this work have also checked their data with respect to the widely applied REFPROP reference database [27], obtaining results which are summarized in Table III. It should be noted that the performance of the proposed model for these systems is quite uniform and, in general, reliable.

**Table III.** Accuracy Results Reported in Ref. [19] Applying REFPROP [27] for the Data Calculation

| Mixture | Range $T$ (K) | Range $\rho$ (mol $L^{-1}$) | NPT | AAD (%) | NPT | AAD (%) | NPT | AAD (%) | Ref |
|---|---|---|---|---|---|---|---|---|---|
| | | | Liquid | | Vapor | | | | |
| | | | | | Steady-state | | Transient | | |
| R134a/R290 | 243–348 | 0.037–12.3 | 411 | 5.53 | 290 | 8.70 | 284 | 5.27 | [19] |
| R32/R290 | 229–347 | 0.012–17.0 | 295 | 6.82 | 418 | 16.83 | 534 | 11.58 | [19] |

## 4. CONCLUSIONS

The TC surfaces of mixtures of halogenated alkanes are calculated using a predictive model based on an improved analysis of a "*conformality*" concept carried out for pure fluids in previous work [14]. The required inputs for each of the mixture components are the critical parameters $T_c$, $P_c$, a TC experimental value for the liquid phase, and a dilute-gas term individual correlation. Since no information is required for the mixture, the resulting mixture model can be considered as *predictive*. Making use of two reference fluid TCDEs, the model can be applied over the whole $\lambda PTx$ surface, only excluding a region very close to the critical point. Different kinds of mixing rules are used for the model; the Mason and Saxena mixing rules are particularly effective for the dilute-gas term contributions, while those of Wong et al. are quite suitable for the excess term.

The model is first applied to the regular mixtures R32/R134a, R125/R134a, R32/R125, R134a and R404a. On a total of 3581 experimental points, including liquid and vapor phases, the overall AAD is 3.58%. Considering that this prediction accuracy is comparable with that of the dedicated equations for pure fluids, the proposed approach can be regarded as satisfactory, taking into account that these results are obtained in a predictive mode.

For azeotropic mixtures the model accuracy becomes dependent on the particular mixture. With weak azeotropy good results are also obtained, but with systems of increasing azeotropic behavior, better results are obtained by using the interaction parameters of the mixing rules for the dilute-gas term, for the excess term, or for both. In these cases it can be verified that only a limited number of experimental mixture data are sufficient to achieve the accuracy level observed for the regular systems. In fact, on a total of 1989 points the overall AAD for the azeotropic mixtures studied, obtained averaging the cases needing correlation of the TC terms and those not needing correlation, is 5.30%.

Besides the satisfactory results of the proposed model, it is demonstrated that general CS methods can be exploited, with particular advantages for those thermophysical properties with scarce available data or where the experimental accuracy levels need to be improved.

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